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SYNTHESIS AND PROPERTIES OF 5-(1,3-DITHIOL-2-YLIDENE)-2(5H)-THIOPHENONE1)

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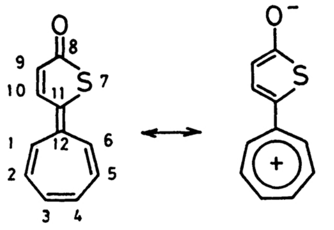
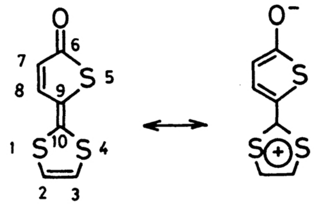
The title compound and its phenyl derivatives have been prepared by the advantageous route which we have developed. These cross-conjugated compounds are suggested to have a preferable contribution of the quinonoid resonance structure at the ground state, but are slightly more polar than the iso-π-electronic 5-cycloheptatrienylidene-2(5H)-thiophenone, revealing that the dithiolidene residue is more electron-donating than the cycloheptatrienylidene one.

A 1,3-dithiolium ion and its simple derivatives, key synthetic precursors for TTF,3) have been studied on their electronic structure in connection with their hetero aromatic character4) and with organic charge-transfer salts of TTF with TCNQ.5) However, the cyclic cross-conjugated compounds having 1,3-dithiolidene residues have not been well discussed regarding to their ground state electronic structures, especially on the question how the dithiolidene residue will differ from the iso-π-electronic cycloheptatrienylidene residue in electron-donating property which induces possible 6π electronic conjugation. In order to estimate the difference in donating properties between dithiolidene and cycloheptatrienylidene residues, it appears desirable to prepare the compounds in which the 1,3-dithiolidene residue and cycloheptatrienylidene residue respectively, enter into conjugation with the same electron acceptable unsaturated moiety. In the preceding paper, we developed an advantageous method for the preparation of the inserted annulenones such as 1.6) On this account, we have now prepared the desirable dithiolidene analogs 2 and 6 (6'), and compared their properties with those of 1, which are reported herein.

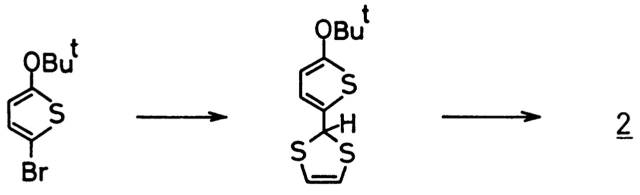


1a 1b

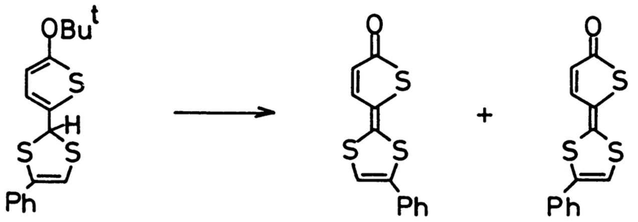


2a 2b

Grignard reaction of the magnesium derivative of 2-bromo-5-t-butoxythiophene (3)7) with 2-methoxy-1,3-dithiol8) in ether gave a dithiolylthiophene derivative 4 [yellow needles, mp 59-60 °C, 38%]. Hydride abstraction of 4 with an equimolar amount of triphenylmethyl fluoroborate in dry dichloromethane at 0 °C, followed by neutralization of the resulting de-t-butylated dithiolium fluoroborate with aqueous sodium bicarbonate, yielded dithiolidenethiophenone 2 as maroon plates [mp 187-188 °C, 32% yield, ν max (KBr) 1635, 1535, 1490, 1185 cm^{-1}; λ max (c-hexane) 225 nm (log ε 3.91), 255 (sh), 267 (3.26), 280 (3.25), 294 (3.15); MS m/e (%) 200 (M^+, 5), 172 (9), 69 (base), 45 (94)], which is stable on exposure to air at room temperature. Similar hydride abstraction of 5 [yellow oil, 57%], obtained by treatment of the magnesium derivative of 3 with 2-methoxy-4-phenyl-1,3-dithiol, gave a 1:1 mixture of phenyldithiolidenethiophenones 6 and 6'.



3 4



5 6 6'

The ^{1}H NMR of the mixture shows singlets at δ 6.65 and δ 6.75 for H-2 and H-3, respectively,[10] in 1:1 integration ratio, which shows no tendency to coalesce even at 30 °C, indicating that an energy barrier is too high to allow rotation about the intercyclic bond of 6 at ordinary temperatures.

The longest wavelength absorption maximum of 2, assignable to the $\pi-\pi^*$ transition along the long molecular axis, is shifted bathochromically by 17 nm from that of 1 in cyclohexane. The absorption maximum of 2 shows a red shift on going from less polar to polar solvents, indicating that the contribution of the quinonoid structure 2a is preferable to the dipolar structure 2b at the ground state by analogy to 1 (Table 1).

Table 1 : The Solvent Effect on the Longest Wavelength Transitions of 1, 2, and a mixture of 6 and 6' λ max nm (log ε)

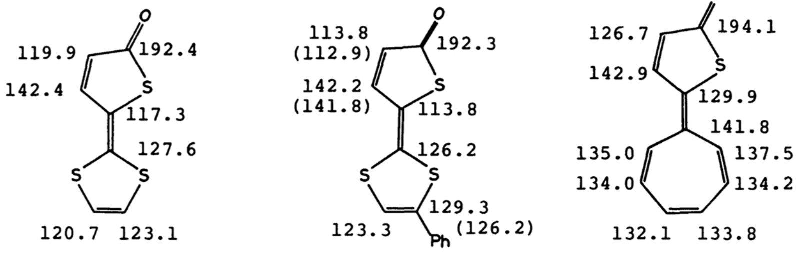
Compound	c-Hexane	Benzene	CH_2Cl_2	Acetone	MeCN	DMSO	Δλ nm
2	444 (4.23)	443 (4.35)	449 (4.33)	447 (4.22)	450 (4.40)	461 (4.40)	+17
6 + 6'	455 (4.32)	456 (4.39)	464 (4.42)	457 (4.43)	459 (4.42)	469 (4.43)	+14
1	427 (4.40)	——	——	435 (4.39)	437 (4.42)	447 (4.42)	+20

On comparing the ^{1}H NMR chemical shifts of the dithiol ring protons with each other, H-2,3 of 2 (Table 2) are found at lower field by 0.54-0.65 ppm than the corresponding protons of 4, but at higher field by about 1.5 ppm than the ring protons of 2-methylthio-1,3-dithiolium ion (δ 8.1).[11] Therefore, the quinonoid structure 2a, rather than the dipolar structure 2b, contributes predominantly to the ground state of 2. As can be seen in Table 2, the chemical shifts of the ring protons H-7,8 of 2 appears at a little higher field than those of the corresponding protons, H-9,10 of 1. Moreover, the vicinal coupling constant $J_{7,8}$ of 2 is smaller than $J_{9,10}$ of 1. The same trend is observed on comparisons of the chemical shifts and coupling constants of the thiophene ring protons between 6 (6') and 1.

Table 2 : ^{1}H NMR Spectral Data of 2, 6 + 6', 1, and 4 at 100 MHz in CDCl$_3$ δ ppm, J in Hz

Compound	Thiophene residue		1.3-Dithiol residue	
2	6.08 d H-7 7.55 d H-8	$J_{7,8}$ = 5.8	6.57 d H-2 6.68 d H-3	$J_{2,3}$ = 6.5
6 + 6'	6.10 d H-7 7.55 d H-8 7.57 d	$J_{7,8}$ = 5.6	6.65 s H-2 6.75 s H-3	
1	6.17 d H-9 7.83 d H-10	$J_{9,10}$ = 6.0	6.95 6.70 H-1,6 6.30 6.00 H-2 H-5	
4	6.13 d H-3 6.68 dd H-4	$J_{3,4}$ = 4.0	6.03 s 2H 6.18 d 1H	J = 0.8

The ^{13}C NMR spectral feature shown in Fig. 1 gives a more clear insight into the electron densities of the ring carbons of the thiophene residues. The chemical shift of C-7 of 2 appears at higher field by 6.8 ppm than that of the corresponding C-9 of 1. The higher field shifts are also observed in the chemical shifts of C-6 and C-8 of 2 on comparing with C-8 and C-10 of 1, respectively, although the differences become smaller.



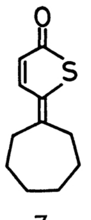
2 6 (6') 1

Fig. 1 ^{13}C NMR chemical shifts of 2, 6 (6'), and 1 in CDCl$_3$ at 50.3 MHz
Chemical shift assignments of the 7-membered ring carbons of 1 are interchangeable

From these results it is suggested that the electron-donating property in the dithiolidene residue of 2 is a little higher than that of the cycloheptatrienylidene residue of 1. This is further supported by the experimental dipole moments (Table 3) of 2 and 1, the former value being larger by 0.1 D than the latter one, although the distance between the oxygen atom and the center of the terminal ring is about 0.3 Å shorter in 2 than in 1.

Table 3 : Experimental Dipole Moments of 2, 1, and 7

Compound	2	1	7
μ (D)	6.0	5.90	5.16



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These experimental dipole moments supply the most direct quantitative measure of the dipolar structures (2b and 1b) contribution in the ground state. Both 2 and 1 exhibit larger dipole moments than a reference compound 7, neverthless, the dipole moment differences between 2 and 7 ($\Delta\mu$ = 0.84 D) and between 1 and 7 ($\Delta\mu$ = 0.74 D) are too small[6] to evaluate the significant charge separation in the ground states of 2 and 1. This is fully consistent with the consideration of the preferable polyolefinic character obtained from spectroscopic analyses mentioned above.

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7) Compound 3 was obtained through the Grignard reaction of the magnesium derivative of 2,5-dibromothiophene with t-butylperbenzoate.
8) 2-Methoxy-1,3-dithiol was obtained from 1,3-dithiolium ion by a similar method for preparation of 7-alkoxycycloheptatriene from tropylium ion.[9] A solution of 1,3-dithiolium ion in methanol was neutralized by sodium bicarbonate. Colorless liquid (95%), bp 60-61 °C/8 mmHg, ^{1}H NMR ($CDCl_3$) δ 3.17 (OMe), 6.32 (2H, s), 6.98 (1H, s).
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